TABLE 1 — ADDUCTS OF ACRIDINE AND PIPERAZINE

Adduct	m.p.	Found (%) (Calc.)	
	°C	N	X
$TiCl_4$-Acr	235	4·06 (3·80)	38·62 (38·91)
$SnBr_4$-Acr	246*	2·41 (2·26)	51·20 (51·71)
SnI_4-Acr	177	2·10 (1·73)	63·62 (63·20)
$(TiCl_4)_2$Ppr	300*	5·99 (6·20)	30·03 (30·40)
$SnBr_4$-Ppr	283*	5·41 (5·34)	62·01 (61·60)
SnI_4-Ppr	350*	4·21 (3·90)	71·68 (71·30)

Acr = acridine; Ppr = piperazine
*Melted with decomposition.

at 1590, 1625; 1575, 1630; and 1575, 1640 respectively. It is known that coordination through the nitrogen atom of the pyridyl group[11] causes an increase in the C=N stretch. It is noteworthy that this shift in the Sn(IV) halide adducts increase with increasing halogen size and is smallest for Ti(IV) chloride adducts. All the complexes are thus suggested to have a trigonal bipyramidal geometry. However, the possibility of a hexacoordinated structure with halide bridging could not be ruled out.

In the far IR spectrum the acridine complexes of $TiCl_4$ show two strong bands at 410 and 460 cm^{-1} and a weak band at 375 cm^{-1} which may be due to Ti-N and Ti-Cl bands.

Molar conductances of piperazine adducts could not be measured owing to their insolubility in organic solvents.

A comparison of IR spectra of piperazine and its complexes shows appreciable negative shift in the νN-H; from 3328 cm^{-1} in the ligand to 3150, 3000 and 3080 and 3300 cm^{-1} in adducts with $TiCl_4$, $SnBr_4$ and SnI_4 respectively. An increase in the C=N stretching frequency from 1444 cm^{-1} in the free ligand to 1460, 1480 and 1450 cm^{-1} in the adducts with $TiCl_4$, $SnBr_4$ and SnI_4 respectively is also observed. The decrease in the νN-H is attributed to coordination of Sn(IV) or Ti(IV) with the nitrogen atom of piperazine. The 1:2 complex of $TiCl_4$ with piperazine[12] may assume a five-coordinated binuclear structure by coordinating with two $TiCl_4$ molecules through the nitrogen atoms of a piperazine molecule. Two distinct bands at 378 and 365 cm^{-1} in the far IR region have been observed and assigned to Ti-Cl bond.

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Complexes of Re(IV) with 2-Hydroxy- & 8-Hydroxy-quinolines & *o*-Phenanthroline

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2-hydroxy- and 8-hydroxy-quinolines and *o*-phenanthroline initially form compounds of the types H_2 [hydroxyquinoline)$_2$ReCl$_6$] and H_2 [(o-phen)$_2$ReCl$_6$] respectively with potassium hexachlororhenate(IV). On reaction with excess ligands, these compounds are converted into the corresponding hydroxo complexes of the types Re(OH)Cl(oxyquinoline)$_2$ and Re(OH)Cl$_3$-(*o*-phen). The compounds are paramagnetic with μ_{eff} = 2·1-3·78 BM indicating a quadrivalent state for Re in these compounds.

IN continuation of our earlier work[1-3] on Re(IV and V) complexes of pyridine and picolines, further work on the complexes of Re(IV) with hydroxyquinolines and *o*-phenanthroline is reported in this note.

Re(IV) complexes with hydroxyquinolines — Two types of compounds were formed with 2- and 8-hydroxyquinolines. H_2[(2-hydroxyquinoline)$_2$-ReCl$_6$] and H_2[(8-hydroxyquinoline)$_2$ReCl$_6$] were obtained as yellow crystalline solids on mixing an aqueous solution of hexachlororhenate[4] (1 g) with the respective hydroxyquinolines (1·5 g) dissolved in dilute acetic acid. The solid obtained in each case was filtered, washed and dried over fused $CaCl_2$. The compounds are almost resistant towards dilute acids but turn black on treatment with alkali.

The hydroxochloro-bis(oxyquinoline) Re(IV) complexes, [Re(OH)Cl(2-oxyquinoline)$_2$] and [Re(OH)Cl-(8-oxyquinoline)$_2$], were formed when the respective yellow hydroxyquinoline salts were warmed with excess of the respective hydroxyquinolines in acetic acid (0·1*M*) on a water-bath. The precipitate separated in each case was filtered, washed and dried *in vacuo*.

The compounds are insoluble in water or ethanol but completely dissolve in boiling nitrobenzene. The compounds did not suffer any loss in weight on heating to 130°. These are non-conducting in nitrobenzene.

TABLE 1 — COLOUR, ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES

Compound	Colour	Analyses (%), Found (Calc.)			μ_{eff} (BM)
		Re	N	Cl	
H_2[(2-Hydroxyquinoline)$_2$ReCl$_6$]	Yellow	26·61 (26·87)	4·02 (4·04)	30·77 (30·74)	3·78
Re(OH)Cl(2-L)$_2$	Dark snuff	34·88 (35·26)	5·24 (5·30)	6·78 (6·72)	3·1
H_2[(8-Hydroxyquinoline)$_2$ReCl$_6$]	Yellow	26·58 (26·87)	4·02 (4·04)	30·81 (30·74)	3·72
Re(OH)Cl(8-L)$_2$	Black	35·28 (35·26)	5·28 (5·30)	6·75 (6·72)	3·25
H_2(*o*-Phenanthroline)$_2$ReCl$_6$	Yellow	22·9 (23·34)	7·18 (7·02)	27·02 (26·71)	2·85
Re(OH)Cl$_3$(*o*-phen)	Black	36·19 (36·68)	5·82 (5·51)	21·21 (20·97)	2·1

LH = Hydroxyquinoline.

Re(IV) complexes with o-phenanthroline — Two types of compounds were formed with *o*-phenanthroline also. H_2[(*o*-phenanthroline)$_2$ReCl$_6$] was prepared in a similar manner as the corresponding hydroxyquinoline salt except that orthophenanthroline was taken in conc. HCl instead of acetic acid. The compound is insoluble in water but gradually decomposes with separation of ReO_2 on warming with alkali.

The hydroxo-trichloro(*o*-phenanthrolinato) Re(IV) complex, [Re(OH)Cl$_3$(*o*-phen)], was formed when an ethanolic solution of *o*-phenanthroline (2 g) was added to an aqueous solution of potassium hexachlororhenate (IV) (1 g) and the mixture warmed on a water-bath for 1 hr. The precipitate obtained was filtered, washed and dried over fused $CaCl_2$. The compound is insoluble in water and sparingly soluble in nitrobenzene. There is no loss in weight on heating up to 130°. It is non-conducting in nitrobenzene.

For elemental analyses, a weighed sample of the complex was fused with sodium peroxide and sodium carbonate. Rhenium and chloride were estimated from the aqueous extract as nitron perrhenate and silver chloride respectively. Nitrogen was estimated by Dumas' semimicro method.

Bulk magnetic susceptibility was measured using the Gouy method. Infrared spectra (nujol mull) were recorded on a Perkin-Elmer double beam spectrophotometer model 21. Visible spectra were measured on a Hilger-Uvispek spectrophotometer and conductances on a Phillips conductivity bridge. The analytical and magnetic moment data are given in Table 1.

All these compounds are paramagnetic (μ_{eff} = 2·1-3·78 BM) and exhibit two absorption maxima in the regions 370-395 and 432-460 nm respectively. Thus, in these compounds rhenium is present in the quadrivalent state. IR spectra of the compounds Re(OH)Cl(oxyquinoline)$_2$, and Re(OH)Cl$_3$(*o*-phen) show a characteristic absorption band around 950 cm^{-1} which may be ascribed to (Re-OH) stretch[5].

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Complexes of Arginine, Histidine, Lysine & Isoleucine with Potassium Hexacyanoferrate(III)

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Arginine, histidine, lysine and isoleucine react with potassium hexacyanoferrate(III) at *p*H 10·85, 7·0, 8·0 and 9·1 respectively under UV irradiation to give brown or yellowish brown products. Spectrophotometric and polarographic studies show the formation of 1 : 1 complexes. Infrared data show that the amino acid is bound to iron through nitrogen of the amino group and oxygen of the carboxylic group.

THE decomposition of hexacyanoferrate (II) on irradiation with UV light and substitution of the cyano groups by organic bases have been reported[1,2]. Since reactions involving amino acids and metal cyanides can be of physiological importance due to the known inhibition[3] of certain enzymes by cyanides, Malik and Aslam[4,5], reported the interaction of amino acids and hexacyanoferrate (II). However, the corresponding reactions of amino acids with hexacyanoferrate (III) have not been reported so far. Studies were, therefore, undertaken to study the interaction of histidine, arginine, lysine and isoleucine with hexacyanoferrate (III).

Solution of potassium hexacyanoferrate (III) (Analar, BDH) was prepared in conductivity water.